REMARKS

The application has been amended and is believed to be in condition for allowance.

Claims 1-12, and 23-25 remain in this application. Claims 13-18, 21-22 are withdrawn. Claims 6-7 and 19-20 are canceled.

An English translation of A.P.Garshin et al., "Abrazivnye materialy", 1983, Mashinostroenie (Leningrad) is provided as an appendix to this response for the Examiner's convenience. Entry of the translation is respectfully requested.

The Official Action rejected claims 1-5, 8-9 and 12 under 35 USC 102(b) as being anticipated by Nikitina et al. (US 4,906,255; hereinafter "NIKITINA").

The Official Action rejected claims 10-11 and 23-25 under 35 USC 103(a) as being unpatentable over NIKITINA.

The rejections are respectfully traversed for at least the reasons that follow.

As to claim 1, it is respectfully submitted that NIKITINA does not teach or suggest the requirement of the maximum carbon content being 200 ppm.

The Official Action states on page 3 that NIKITINA teaches no <u>addition</u> of carbon to the mixture before arc melting is carried out; therefore, this would indicate that no carbon, or at least not an appreciable amount, would be in the fused grains.

The Official Action concludes that the carbon amount would be below 200 ppm and accordingly maintains the rejection of claim 1.

Applicant respectfully disagrees. Although NIKITINA does not explicitly describe the oxidation-reduction conditions in which the abrasive material is produced, NIKITINI refers to the "conventional manner" wherein aluminum oxide is melted in an electric arc furnace with additions containing one or more listed oxides, referring specifically to the reference A.P.Garshin et al., "Abrazivnye materialy", 1983, Mashinostroenie (Leningrad) (hereinafter, "GARSHIN"; see NIKITINA, column 4, lines 27-31; also, column 2, lines 20-25; column 2, lines 62-63).

Contrary to the Official Action's position that no addition of carbon is taught by NIKITINA, GARSHIN teaches the use of a furnace "fitted with graphitised (sic) electrodes" (GARSHIN page 1, lines 3-4). The carbon in the final product may come from an addition of carbon in the starting charge, and also from the consumption of the graphitized electrodes. Thus, an appreciable amount of carbon to exceed 200 ppm is present in NIKITINA even if no other carbon is added.

GARSHIN also teaches oxidizing conditions. From page 1 to 5 of the translation, GARSHIN describes the melting step to obtain white corundum. It is respectfully submitted that one of skill in the art would readily understand that white corundum is manufactured under oxidizing conditions. The white color of refractory products normally corresponds to oxidizing conditions.

Further, GARSHIN recites that "the most effective technical solution in order to increase the quality of the final product was found to be processing of the melt stream with compressed air outside the furnace, which ensures homogenisation (sic) of the melt, and an increase in its temperature owing to oxidative processes," (GARSHIN, page 2, last paragraph and page 3, first paragraph). "[A] still higher quality crystallised (sic) product can be ensured by blowing oxidizing gases through the whole mass of the melt through a bottom of the mould or of an intermediate vessel," (GARSHIN, page 3, first paragraph). These passages of the reference to NIKITINA confirm that oxidation is not only disclosed, but also advantageous.

According to the method of the present invention, the melting energy before casting ranges "between 2000 and 2500 kWh per ton of said mixture of raw materials" (specification, page 3, lines 22-23; see also claim 13). This very high melting high energy also contributes to the decrease of the carbon content.

In contrast, the method of NIKITINA, as disclosed by GARSHIN, describes a melting step wherein the melting energy is "within the range 1200 to 1300 kWh/ton of fragments," (GARSHIN page 1, third paragraph, line 2). One of skill would not expect that with such a low melting energy as described by GARSHIN that NIKITINA could reach a carbon content less than 200 ppm, especially if reducing conditions are further disclosed.

Therefore, it is respectfully submitted that NIKITINA fails to teach or suggest a carbon content being 200 ppm as required by claim 1. NIKITINA, by reference to GARSHIN, at least teaches a source of carbon by way of the graphitized electrodes, and the carbon content in the final product is therefore higher than 200 ppm as a result of the oxidizing conditions disclosed in GARSHIN as explained above.

Further, the teachings of GARSHIN relating oxidizing conditions to a superior product would lead one of skill towards oxidizing conditions, and therefore, to carbon contents higher than 200 ppm (corresponding to strong reducing conditions). Therefore, it is respectfully submitted that NIKITINA teaches one of skill <u>away</u> from the claimed invention.

Reconsideration and withdrawal of the rejection are respectfully requested.

It is also respectfully submitted that independent claim 25 is patentable at least for the same reasons set forth above as to claim 1, and claims depending from claim 1 are patentable at least for depending from a patentable.

In addition, as to claim 9, it is respectfully submitted that NIKITINA does not teach or suggest grains which <u>consist</u> of corundum crystals <u>surrounded</u> by a nonstoichiometric $MgO-Al_2O_3$ spinel phase.

The Official Action acknowledges that NIKITINA is silent to the stoichiometry or nonstoichiometry of the spinel

phase, but asserts that NIKITINA would be inherently <u>at least partially</u> nonstoichiometric.

Respectfully, this does not teach what is claimed. That is, claim 9 does <u>not</u> recite grains which <u>comprise</u> corundum crystals surrounded by a nonstoichiometric MgO-Al2O3 spinel phase. Claim 9 requires grains which <u>consist</u> of corundum crystals surrounded by a nonstoichiometric MgO-Al2O3 spinel phase. In other words, claim 9 relates to a structure wherein the spinel phase is <u>substantially completely nonstoichiometric</u>.

The teaching of only partially nonstoichiometric, inherent or express, does not anticipate claim 9. It is therefore respectfully submitted that claim 9 is novel and non-obvious over NIKITINA. Reconsideration and withdrawal of the rejection are respectfully requested.

Further as to claims 10, 11, and 23-25, it is respectfully submitted that it would have not been obvious to one of ordinary skill in the art, through ordinary experimentation and optimization, to arrive at a material based on example 10 of Table 1 of NIKITINA.

The Official Action offers NIKITINA's Abstract to argue that NIKITINA teaches a broad range of corundum crystal sizes, and further argues that "ordinary experimentation and optimization" would arrive at a material corresponding to that recited in claims 10, 11, 23-25, based on the disclosure offered

in part to anticipate claim 1: NIKITINA page 5, Table 1, composition 10.

On the contrary, NIKITINA clearly teaches example 10 of Table 1 as <u>disadvantageous</u> where "the abrasiveness of the grain decreases considerably," (column 6, lines 1-2). The composition as recited in the present invention would be <u>unexpected</u> to one of skill based on this disclosure teaching <u>away</u> from the composition of example 10, thereby <u>discouraging</u> experimentation on this composition. Accordingly, it is respectfully submitted that the invention as claimed in claims 10, 11, and 23-25 are non-obvious over NIKITINA.

From the foregoing, it will be apparent that the applicant has fully responded to the March 19, 2008 Official Action and that the claims as presented are patentable. In view of this, applicant respectfully requests reconsideration of the claims, as presented, and their early passage to issue.
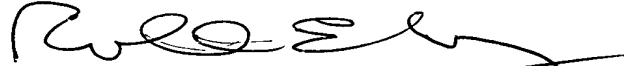
In order to expedite the prosecution of this case, it is requested that the Examiner telephone the attorney for the applicant at the number set forth below if the Examiner is of the opinion that further discussion of this case would be helpful.

The Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any

overpayment to Deposit Account No. 25-0120 for any additional

fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17.

Respectfully submitted,

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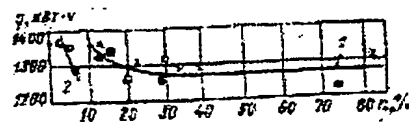   (703) 979-4709

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APPENDIX:

The Appendix includes the following item(s):

☒ English translation of A.P. Garshen et al., "Abrazivnye materially", 1983, Mashinostroenie (Leningrad)

1

Technology for Melting of White Electro corundum. The melting of white electro corundum is effected in three-phase electric refining furnaces, supplied from three-phase transformers of power 4.5 to 6.5 MVA. The furnaces are fitted with graphitised electrodes and have a tilting mechanism. The furnace crown is a sectional, water-cooled structure, from the inside of which there is applied a refractory lining. It is equipped with apertures for the electrodes, for servicing of the furnace throat, charging of alumina, and removal of furnace gases and dust to the electrostatic filters. There is forced water cooling of the crown, casing and bottom of the furnace.

White electro corundum gravel (less than 10 mm) and fragments (100 to 160 mm) are laid successively in 150 to 200 mm layers on the bottom of the casing to a height of 1 m. Then an artificial lining slag of electro corundum fragments (100 to 150 mm), interspersed with the gravel, is spread along the vertical walls up to the top of the casing of the furnace. After this, the crown is mounted on the furnace, and alumina is fed into it in a layer up to 100 mm, on which the firing is performed. During the furnace firing period, alumina is added in portions every 20 to 40 minutes with allowance made for immersion of the electrodes 200 to 300 mm into the alumina. Half an hour before the first pouring of the melt, the furnace is switched off for consolidation of the lining slag. The crystallised product after cooling is fragmented to 300 to 400 mm fragments in an impact machine and sent for grinding.

The specific electric power consumption for the melting of the white electro corundum varies within the range 1200 to 1300 kWh/ton of fragments and depends on the properties of the starting alumina. In studies carried out by V Ya Abramov, it was established that the optimal content of α-Al_2O_3 in the alumina must be not less than 25 weight % (Fig. 2.11). On increasing the content of α-Al_2O_3 in the alumina from 10 to 30 weight %, the specific electric power consumption decreases correspondingly from 1370 to 1270 KWh/ton. According to the results of subsequent studies, the changeover to electric furnaces for the melting of highly calcined alumina (content of α-$Al_2O_3 \leq 75$ weight %) enables an increase in the stability of the lining slag and a decrease in the specific electric power consumption from 1300 to 1240 kWh/ton. At the same time, it was established that the carry-over of dust from the electric furnaces into the electrostatic filters decreased from 135 to 70 kg/h.

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y axis: q, kWh; x axis: n, %.

Fig. 2.11 Change in specific electrical power consumption q in the melting of alumina as a function of the content n of α-Al$_2$O$_3$ (the content of the impurities Na$_2$O, Fe$_2$O$_3$, SiO$_2$ and magnetic material in the alumina is 0.51, 0.14, 0.25 and 0.26 weight % respectively) and differing particle size (X: 25-28; O: 28-30; ●: 30-32; ■: 32-34; ▲: 34-36; △: 36-38); 1. for pure alumina; 2. with addition of corundum production wastes (fraction – 160 μm).

The specific power consumption values are influenced by the design features of the electric furnaces and the electrical melting operating conditions. In studies carried out by B M Tankhel'son, it was established that with the same electrical operating conditions, depending on the diameter of the electrodes, the furnace bath is in different states as regards the power distribution in the melt and in the arc, which results in a different level of power consumption and lining slag condition.

From the time of the changeover to the pouring process, the researchers' efforts were directed towards the search for conditions ensuring a crystalline structure analogous to that for the "block" process during the cooling of the melt. One of the technological solutions in this approach was the proposal of secondary electrical heating of the melt in the mould. However, industrial experience of the use of this technology showed that, apart from an increase in the specific electric power consumption, no significant improvement in the quality of the white electro corundum is observed. V A Alferov and I V Lavrov, studying the quality of the white electro corundum on changing to a continuous melting method, indicated the possibility of obtaining a structure analogous to the structure of the block product with an increase in the mass of the ingots to 25 tons. However, such a large ingot weight is attended by unwarranted complication of the design of the main units and auxiliary equipment. At present, the mass of the ingots is 4 to 7.5 tons, and the ingots of weight 7.5 tons make it possible to improve the quality of the product and the industrial and economic parameters. Thus, the yield of abrasive granules rises from 64 to 65.6%, the whiteness increases from 61 to 73%, and the electric power consumption decreases by 10 kWh/ton.

The most effective technical solution in order to increase the quality of the final product was found to be processing of the melt stream with compressed air outside the furnace, which

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ensures homogenisation of the melt, and an increase in its temperature owing to oxidative processes. As a result of this, the lower part of the ingot (ca. 1/3 of the volume) is character-ised as a monocrystalline product of granule size 0.1 to 0.5 mm, while dendritic crystallisation is observed in the remaining zones. Here it is precisely the fine-grained product which has increased purity and good physical and mechanical properties. A still higher quality crystallised product can be ensured by blowing oxidising gases through the whole mass of the melt through the bottom of the mould or of an intermediate vessel.

Structure and Quality of the Abrasive Materials

In accordance with the industry standard, white electro corundum abrasive materials must satisfy the requirements indicated in Table 2.17.

Таблица 2.17. Требования отраслевого стандарта к шлифматериалам электрокорунда белого

Показатель	Марка и зернистость, мкм															
	25А			24А						23А					
	800–160	120–60	50–40	800–160	120–60	50–40	63–50	40–14	10–5	800–160	120–60	50–40	63–50	40–14	10–5
Массовая доля, % (не более):															
Fe₂O₃	0,02	0,03	0,08	0,05	0,05	0,03	0,03	0,04	0,05	0,10	0,12	0,12	0,05	0,07	0,10
SiO₂	0,10	0,12	0,12	0,14	0,16	0,16	0,15	0,15	0,25	0,20	0,20	0,35	0,35	0,20	0,30
Na₂O	0,20	0,25	0,25	0,30	0,35	0,35	0,30	0,40	0,50	0,40	0,50	0,50	0,40	0,50	0,60
C	0,10	0,15	0,15	0,15	0,20	0,20	0,15	0,15	0,15	0,20	0,25	0,25	0,15	0,20	0,25
магнитный материал	0,008	0,005	0,009	0,01	0,01	0,01	0,007	0,007	0,007	0,15	0,15	0,13	—	0,13	0,13
Зернистость, мкм	800	630	500	400	320	250	200	160	120	100	80	60	—	50	40
Насыпная масса, ρм·10³, кг/м³	1,87	1,87	1,84	1,82	1,80	1,79	1,79	1,72	1,70	1,68	1,66	1,68	—	1,56	1,66

Table 2.17 Requirements of industry standard for white electro corundum abrasive materials

Column: 1. parameter; 2. brand and granularity, μm.

Row: 1. content, weight % (not greater than); 2. magnetic material; 3. granularity, μm; 4. bulk density, $\rho_m \times 10^3$, kg/m³.

The carbon content and the bulk density parameter are determined for the accumulation of statistical data and are used as reference characteristics.

The magnetic material content is determined in accordance with the industry standard at each granularity level.

The destructibility and abrasive power are monitored only for abrasive materials in the high quality category.

4.

I V Lavrov, studying white electro corundum, found a number of types of grain structure (Table 2.18).

Т а б л и ц а 2.18. Строение зерен белого электрокорунда

| Строение зерна | Массовая доля зерен, % | | | | | | | | σ_{р.з} (зернистость 40), Н/зерно |
| | 1-я проба | | 2-я проба | | 3-я проба | | 4-я проба | | |
	под МБС	иммерсионным методом	под МБС	иммерсионным методом	под МБС	иммерсионным методом	под МБС	иммерсионным методом	
Монокристальное	89	85	83	70	85	83	86	76	26,20±1,50
Мозаичное	—	8	—	17	—	12	—	17	22,50±1,20
Дендритное	6	—	9	—	13	—	7	—	23,40±1,75
Плотные агрегаты	—	—	5	—	2	1	3	—	22,66±2,30
Неявные агрегаты	—	2	—	4	2	2	—	1	18,60±4,35
Агрегаты	5	5	3	9	—	2	4	6	12,95±3,75

Table 2.18 Structure of white electro corundum grains

Column: 1. grain structure; 2. content of grains, weight %; 3. 1st, 2nd, 3rd and 4th samples: a. under MBS, b. by immersion method; 4. $\sigma_{e.g}$ (granularity 40), N/grain

Row: 1. monocrystalline; 2. mosaic; 3. dendritic; 4. dense aggregates; 5. indistinct aggregates; 6. aggregates.

It is not difficult to see that the greatest stability and destructive load correspond to grains of monocrystalline structure, while other structural forms have both a lower absolute strength value and a much greater range of variation.

A particularly undesirable impurity in white electro corundum is iron, present in oxide form as a result of the interaction of the melt with the walls of moulds or as a product of milling during grinding of the electro corundum in rod mills.

During the processing of the fragments into abrasive materials under the action of water and temperature (calcining), the iron impurities may adopt nonmagnetic forms, which in the final analysis during the heat treatment of abrasive products leads to the appearance of spall or so-called midges on the tool.

5.

Although not regulated by an industry standard, an extremely important aesthetic parameter for white electro corundum is the "whiteness", characterised by the reflection coefficient of the electro corundum grain to incident light. As was shown by I Ya Rivlin, the grey colour of electro corundum, white by nature, is neutral achromatic, and consequently arises owing to the presence of black or grey impurities in the white material. It is considered that the grain has a sugar-white colour at a reflection coefficient of 65-75%, white at 50-60%, light grey at 45-50%, grey at 30-45% and dark grey at below 30%. Without denying the effect of various factors on the colour of white electro corundum, we consider that the main cause of darkening of white electro corundum is nonstoichiometry of the α-Al_2O_3 with regard to oxygen, in connection with which oxidative refining treatment of the melt with gases seems to be the most effective means of improving the commercial appearance of the product and articles made from it.

2.4 Alloyed Electro Corundums

Alloyed electro corundums include materials obtained by melting of alumina with the addition of oxides forming isomorphic solid solutions with α-Al_2O_3 on crystallisation of the melt. First and foremost among such oxides are Cr_2O_3, TiO_2 and V_2O_3. For alloying with titanium and vanadium, TiO_2 and V_2O_5, which under reducing melt conditions are readily converted to Ti_2O_3 and V_2O_3, are used.

Requirements for abrasive materials of chromium electro corundum are specified in an industry standard (Table 2.19). Electro corundum alloyed with chromium and titanium is produced as two brands, 91A and 92A, depending on the technical conditions. The content of titanium in electro corundum alloyed with chromium and titanium is 1-2 weight %.

6.

Таблица 2.19. Требования отраслевого стандарта к шлифматериалам хромистого электрокорунда

Марка	Зерни-стость	Массовая доля компонента, %							
		Fe_2O_3 не более	общая Cr_2O_3	Cr_2O_3 в твердом растворе, не менее	$Cr_{св.}$ не более	Na_2O	SiO_2	C	маг-нит-ного мате-риала
						не более			
34A	80—16	0,10	0,8—1,25	0,50	0,20	0,40	0,10	0,15	0,020
	12—6	0,12	0,5—1,50			0,50	0,20	0,20	0,025
33A	80—16	0,12	0,5—2,0	0,50	0,30	0,50	0,15	0,20	0,025
	12—6	0,15	1,0—2,0			0,60	0,25	0,30	0,030

Примечание. Показатель C не является критерием качества материала и служит для накопления статистических данных.
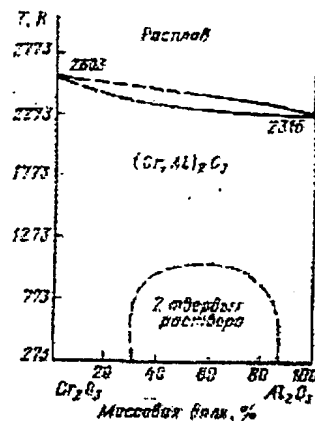
Table 2.19   Requirements of industry standard for abrasive materials of chromium electro corundum

Column: 1. brand; 2. granularity; 3. mass content of component, %; не более = not greater than; общая = total; в твердом растворе, не менее = in solid solution, not less than; магнитного материала = of magnetic material.

Note: The parameter C is not a material quality criterion and serves for the accumulation of statistical data.

In the system Al_2O_3-Cr_2O_3 (Fig. 2.12), the liquidus and solidus curves form an extremely simple diagram, characteristic for a continuous series of solid solutions, forming at high temperatures. It has been shown that with a mole fraction of Cr_2O_3 in the solid solution of up to 8%, the constants of the unit cell have a constant value, while at a higher content they vary linearly depending on the concentration of Cr_2O_3. The solid solutions (Al, Cr)$_2O_3$ with a content of Cr_2O_3 up to approximately 10% have a red colour (rubies), while with a higher content thereof they take on a green tint. The colour of the solid solutions also depends on the temperature, this being due to mutual interaction of the atoms (ions) of chromium.

7.

расплав = melt; 2 твердых раствора = 2 solid solutions; массовая доля = mass content

Fig. 2.12 Phase diagram for the system $Cr_2O_3 - Al_2O_3$.

Under the conditions of the electric arc melting of chromium electro corundum, carbon, which has an effect on the completeness of introduction of Cr^{3+} ions into the solid solution, is present in the melt.

Studies carried out by V Ye Gladkov on the magnetic susceptibility (X_T) of high-alumina samples of the Al_2O_3-Cr_2O_3 system with addition of carbon in different amounts in the mixture showed that it differs by ΔX from that calculated according to the law of P Curie. This is determined by the fraction of chromium ions that has not entered into the solid solution, and is calculated according to the equation

$$\frac{\Delta X}{X_T} = 1 - \frac{N_{T.p}}{N_\Sigma},$$

where N_Σ and $N_{T.p}$ are the total quantities of chromium ions in the material and in the solid solution. Processing of the experimental data according to the said equation made it possible to obtain the values of the Cr_2O_3 concentrations in the solid solution (Table 2.20).

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Таблица 2.20. Массовая доля Cr_2O_3 в твердом растворе при различном содержании углерода

Массовая доля Cr_2O_3 в исходной шихте, %	Расчетная массовая доля Cr_2O_3 в твердом растворе при различном содержании углерода, %			
	0	0,1	0,3	0,6
0,75	0,70	0,68	0,67	0,47
1,5	1,36	1,34	1,25	0,80
2,25	1,987	1,89	1,91	1,22
3,0	2,61	2,43	2,46	2,25

Table 2.20 Content of Cr_2O_3 in solid solution at different carbon content

Column: 1. content of Cr_2O_3 in starting mixture, weight %; 2. calculated content of Cr_2O_3 in solid solution at different carbon content, weight %.

The results of the measurements and calculations carried out show that even in samples not containing carbon, thermodynamic equilibrium is not reached and complete dissolution of the Cr_2O_3 does not take place. With the introduction of carbon into the system, the fraction of chromium atoms not constituting structural elements of the crystal lattice of the solid solution increases, but not directly in proportion to the quantity of carbon introduced into the mixture. This effect appears most strongly when the content thereof is greater than 0.3 weight %, this being due to the possibility of the system dissolving a certain quantity of carbon. Even in those cases when the quantity of carbon introduced into the system is sufficient for complete reduction of chromium (III) oxide according to the reaction $Cr_2O_3 + 3C \rightarrow 2Cr + 3CO$, this does not take place. In view of the fact that in the solid state the zone of homogeneity of chromium (III) oxide lies within the range $Cr_{1.92-2}O_3$, a decrease in the influence of the carbon on the change in the valency of the chromium is also possible, in connection with which the concentration of Cr_2O_3 in the solid solution remains relatively high.

Studies by N I Fomkin and coworkers at VNIIASh demonstrated the influence of the methods of preparation of the mixture and the electrical process parameters on the concentration of chromium ions in the solid solution and the properties of the abrasive materials. With the aim of blocking the processes of reduction of chromium oxide, they proposed a melt on aluminium bichromate with additions of MnO_2, V_2O_5 and TiO_2. Only the last-name additive has found practical application, as a result of which the so-called chromium-titanium electro corundum made its appearance. In our opinion, the most radical means of obtaining alloyed

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electro corundum materials is refining of the melt with oxidising gases, which can be effected industrially during the melting of the materials in tapping furnaces. The addition of a 1.5 weight % TiO_2 content to the mixture during the melting of chromium electro corundum results in an increase in the completeness of introduction of chromium into the solid solution from 50 to 80%. At the same time, the bulk density of the abrasive material and its abrasive power increase. The strength of the individual grains in the chromium titanium electro corundum is also higher by 15-20%.

Wide-ranging industrial trials of a tool based on chromium titanium electro corundum have demonstrated its excellent use characteristics, which were also due to the change from the chromium to the chromium titanium electro corundum melting. The melting of the chromium titanium electro corundum basically is carried out in block furnaces, but industrial trials are also being performed on its production in tapping furnaces with alloying with chromium (III) oxide outside the furnace.

Owing to the scarcity of vanadium (V) oxide, electro corundum alloyed with vanadium has not been developed industrially. According to the results of studies, abrasive material made from vanadium electro corundum has a green colour and can be used for the processing of tungsten and molybdenum tool steels, bearing and other materials of hardness HRC 52-65.

The mineral composition of the alloyed electro corundums differs from white electro corundum only by the presence of carbide and nitride compounds of the alloying component and metallic inclusions thereof.

Certain physical and mechanical properties of alloyed electro corundums, according to VNIIASh data, are presented in Table 2.21, from which it follows that an exact link between the type of alloying oxide, its concentration in the solid solution and the durability characteristics of the material is not observed. The concentration limits of the elements forming a solid solution with corundum do not yet have a strictly scientific basis, and studies in this field must be continued.

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Таблица 2.21. Некоторые физико-механические свойства
легированных электрокорундов

Массовая доля легирующего компонента, %						Свойства шлифзерна			
Cr_2O_3		TiO_2		V_2O_5		$\sigma_{e.з}$ (зернистость 40), Н/зерно	шлифующая способность, г	хрупкость, %	H_μ корунда, ГПа
валовая	в твердом растворе	валовая	в твердом растворе	валовая	в твердом растворе				
1,50	1,20	—	—	—	—	31	0,055	42	24
—	—	1,50	0,70	—	—	30	0,057	46	24
—	—	—	—	1,80	1,40	28	0,051	53	22
2,0	1,65	2,50	1,60	—	—	32	0,061	50	23
0,98	0,80	1,34	0,85	—	—	30	0,058	46	24
1,15	0,95	—	—	2,0	1,7	34	0,054	48	23

Table 2.21 Some physical and mechanical properties of alloyed electro corundums

Column: 1. content of alloyed component, weight %: a. total, b. in solid solution; 2. properties of abrasive grains: a. $\sigma_{e.g}$ (granularity 40), N/grain, b. abrasive power, g, c. brittleness, %; d. N_μ of corundum, GPa.

2.5 Zirconium Electro Corundum

In the last twenty years, processes of powered rough-grinding have become widespread in practical use both abroad and in this country, as the most effective and productive means for smoothing the surface of slabs, ingots and forged pieces. This was mainly made possible by the creation of a new abrasive material, a eutectic melt of alumina and zirconium (IV) oxide of fine-grained structure and the development of a new technology for the manufacture of abrasive tools, withstanding greater forces for pressing the disc to the surface to be processed (up to 10,000 N and above onto the disc).

The first material of the zirconium electro corundum group was an alloy of alumina with added ZrO_2, taken in 9:1 ratio. Somewhat later, materials with a ZrO_2 content of 40 weight %, and later 25 weight %, appeared, and the parameters of articles made of the latter surpassed all previously manufactured tools: the specific productivity of the discs reached 140 kg metal per kg of abrasive, and was stably at the level of 40-60 kg of metal per kg of abrasive.
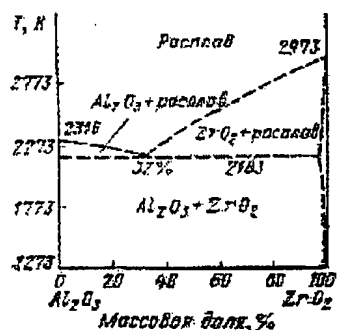
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A tool based on zirconium electro corundum operates especially effectively in the smoothing of high-alloy steels and alloys.

Zirconium electro corundum can be fused from various raw materials. In our country, the melting of zirconium electro corundum is effected from abrasive materials of normal electro corundum and zirconium (IV) oxide in electric arc refining furnaces. A major contribution to the organisation of production of zirconium electro corundum in this country and the study of the abrasive materials obtained from it was made by A S Zubov and I P Vasil'yev.

By now, there are a multitude of technical solutions for the production of zirconium electro corundum, the essence of which basically boils down to methods of crystallisation of the melt, since the main problem in the production of this material is the rapid cooling thereof to temperatures less than 1270 K, ensuring the attainment of a eutectic structure.

To a first approximation, zirconium electro corundum can be regarded as the product of the crystallisation of the binary system $ZrO_2 - Al_2O_3$.

According to the results of G Warterberg, there are no chemical compounds in this system, but at a ZrO_2 content of approximately 40 weight %, a eutectic appears with a melting point of 2193 K. R F Geller detected the presence of a eutectic alloy containing 55 weight % of ZrO_2, with a melting point of 2158 K. According to the results of Japanese researchers, the melting point of the eutectic is 2163 K. A S Berezhnoy constructed a calculated phase diagram for $Al_2O_3 - ZrO_2$ (Fig. 2.13), according to which the content of ZrO_2 in the eutectic alloy is 32 weight %, and its melting point is 2183 K.

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распдав = melt; массовая доля = mass content

Fig. 2.13 Phase diagram for the system $Al_2O_3 - ZrO_2$.

It is unlikely that the insignificant quantities of calcium and magnesium oxides (< 1.0%) present in the zirconium electro corundum can cause the formation of ternary compounds during rapid cooling. For this reason, a decrease in the crystallisation and stabilisation range of high temperature modifications of ZrO_2 due to the presence of the oxides is not to be expected. Magnesium oxide, forming spinel and solid solutions with Al_2O_3, can promote the formation of a fine disperse structure for the material. In the system $Al_2O_3 - ZrO_2 - TiO_2$, there are no ternary compounds, and the lowest melting eutectic melts at 1853 K and has the mass composition (%): $TiO_2 - 60$, $ZrO_2 - 22$ and $Al_2O_3 - 18$.

Additions of SiO_2 and TiO_2 up to contents of 2 and 5 weight % increase the density and strength of zirconium electro corundum cooled in roller crystallisers. The introduction of these oxides into the system somewhat lowers the melting point and promotes the formation of a dense material structure under the conditions of rapid cooling and "welding" of the crystallised incrustations under the pressure of the rollers. Increasing the content of SiO_2 above 2 weight % leads to an abrupt decrease in the strength of the abrasive grains, which is most likely due to the formation of a glassy phase in the crystallised product. At the same time, an increase in the content of titanium (IV) oxide from 1.75 to 5.7 weight % promotes an increase in the strength of the individual grain by almost 20%.

The Ti_2O_3 appearing in the reducing melting process forms a solid solution with the α-Al_2O_3 but the Ti_2O_3 content in this is lower than in normal electro corundum. This circumstance is attended by the formation of a solid solution of TiO_2 in ZrO_2, promoting stabilisation of the high temperature modification of ZrO_2 and wherein the content of TiO_2, more precisely determined with X-ray analysis of samples, is 5.7 weight %.

The introduction of calcium, magnesium and chromium oxides, the content of which is up to 3 weight %, into the composition of the mixture during the melting of zirconium electro corundum, does not cause any significant changes in the microstructure of the material, but increases the strength of the individual grains by 3-6%.

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The microstructure of zirconium electro corundum to a significant degree depends on the cooling conditions. Studies performed by us showed that on increasing the rate of cooling from 12-20 to 1000-2000°C/min, the size of the primary crystals of corundum decreases from 300-400 to 30-10 μm and the number of regions of eutectic structure increases. The primary crystals of corundum as a rule have a shape elongated in the direction of heat removal; zirconium (IV) oxide in the form of baddeleyite surrounds the crystals of corundum or forms eutectic zones. As an example, the microstructures of zirconium electro corundum obtained with different cooling rates are presented in Fig. 2.14.
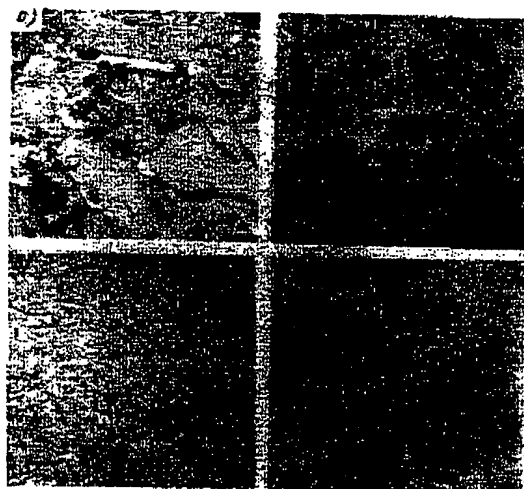

Fig. 2.14 Microstructure of zirconium electro corundum (content of ZrO_2 is 20-25 weight %) with different cooling rates (x 250): a: 12-20°C/min; б: 80-130°C/min; в: 1000°C/min and г: zirconium electro corundum from the "Norton" company (x 500).

Depending on the crystallisation conditions, the properties of the electro corundum also vary considerably (Table 2.22). The change in the durability parameters of the zirconium electro corundum grains is connected with defects in its microstructure. The defectiveness of the structure of the zirconium electro corundum manifests itself in the presence of microcracks between the corundum and the baddeleyite, arising as a result of the shear stresses caused by the difference in the coefficients of thermal expansion of these minerals and possible modification transitions of zirconium (IV) oxide. Since the shear stress at the boundary between crystals is inversely proportional to their total area of contact, a decrease in the size of the crystals will be accompanied by a decrease in the primary stresses and in the probability of occurrence of defects. Baddeleyite, having considerably lower microhardness

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than corundum, enables the latter to absorb shock on application of loads, which substantially raises the brittle fracture limit of the corundum and grains of the material as a structure. With a decrease in the dimensions of the crystals, the load distributes itself more evenly across the volume of the material, as a result of which the resistance to destruction increases. For example, a decrease in the size of the crystals forming the eutectic zones from 150 to 30 μm increases the resistance of the grains of 125 μm size to destruction by a factor of more than two.

Т а б л и ц а 2.22. Некоторые свойства зерен ЭЦ при различных скоростях охлаждения отливок (по данным ВНИИАШа)

$V_{охл}$, °C/мин	$\sigma_{e.в}$ (зерни-стость 125), Н/зерно	Прочность совокупности зерен, %	Насыпная масса, кг/м³	Износостой-кость, мин/мм
8	163	66,0	1910	412
16	197	79,3	1930	470
60	249	83,1	1990	535
170	287	87,0	1970	614
~2000	351	87,0	2030	1200

Table 2.22 Some properties of EC grains at different casting cooling rates (according to VNIISh data)

Column: 1. $V_{cooling}$, °C/min; 2. $\sigma_{e.g}$ (granularity 125), N/grain; 3. grain aggregation strength, %; 4. bulk density, kg/m³; 5. wear resistance, mins/mm.

In industry, the melting of zirconium electro corundum is carried out in three phase electric arc furnaces for the melting of white electro corundum. As mixing materials, technical alumina, abrasive materials of white and normal electro corundums and zirconium (IV) oxide, and as additives, TiO_2, SiO_2 and aluminium metal powder, have proved their worth. From the furnace, the melt passes along an intermediate channel to the ribbon-forming zone, formed by the surface of two rollers (Fig. 2.15), rotating towards one another.
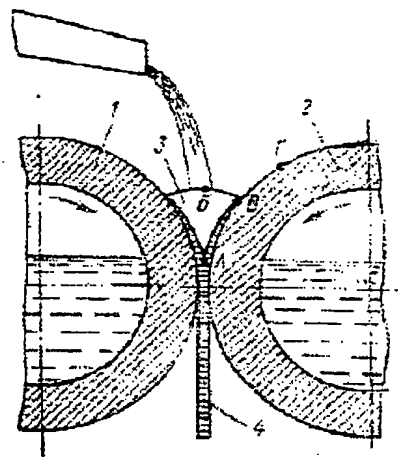
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Fig. 2.15 Diagram of pouring of zirconium electro corundum into roller crystallisers:
1. lead roller; 2. slave roller; 3. wedge of melt; 4. solid strip of electro corundum; A and B:
points of welding and formation of incrustations; Б and Г: temperature measurement points.

The electro corundum melt, arriving in the wedge-shaped space formed by the rollers, spreads along their whole length, at the same time forming "incrustations" on the surface of the water-cooled rollers. The solid incrustations meet at the point A (Fig. 2.15), "weld" into a single strip, and are drawn into the gap between the rollers formed because of the departure of the slave roller from the lead one. The temperature of the melt is 2323-2373 K in the furnace, 2173-2253 K in the stream in the channel, and 2123-2163 K in the zone where the strip is formed (in the wedge of melt between the rollers). The optimal rate of formation of the electro corundum strip on this device is 0.17 m/sec, and the thickness 2.5-3.5 mm. The yield of coarse abrasive grains (2-1 mm) here is 65.3%, while the bulk density changes from 2010 to 1920 kg/m^3.

In view of the scarcity and high price of zirconium (IV) oxide, a baddeleyite concentrate with a ZrO_2 content of 92-94 weight % was tested as the zirconium-containing material.

A comparative characterisation of the zirconium electro corundum grains obtained from different mixing materials and cooled in roller crystallisers is set out in Table 2.23. It can be seen that by using different mixing materials it is possible to obtain a product with rather good mechanical properties. The substantially higher values of the bulk density in imported analogues, irrespective of the lower content of zirconium (IV) oxide therein, can be explained by the difference in the pouring method and the technology for producing the grains. Abroad,

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the crystallisation of zirconium electro corundum is carried out in moulds with the addition of metal spheres or zirconium electro corundum fragments from previous melts into them during the pouring process. The grinding of the material is effected in ball or other mills ensuring a more isometric shape for the grains. It is not possible to obtain an oval grain shape and achieve high values of the bulk weight, nor grains larger than 2.0 mm, from zirconium electro corundum crystallised in the rollers. A further disadvantage of the method of pouring into crystalliser rollers is the low durability and low specific productivity of the rollers.

Таблица 2.23. Характеристика цирконневого электрокорунда, полученного из различных шихтовых материалов

Шихта	Массовая доля компонентов						σр.п (зерни стость (0), Н/зерно	Прочность агрегирования зерён, %	Хрупкость, %	Насыпная масса, кг/м³	Примечание
	ZrO₂	SiO₂	TiO₂	Fe₂O₄	CaO	MgO					
ЭН + ZrO₂ + TiO₂	24,0	0,48	3,50	0,46	0,47	0,06	300	83,0	12.7	2050	Лабораторные образцы
ЭН + бадделент + TiO₂	23,0	0,45	3,42	0,56	—	0,34	395	83,0	11,0	2150	
Глинозём + бадделент + 3.0 % TiO₂	24,7	0,42	3,12	0,17	0,71	—	390	85,0	13,2	2170	Промышленная партия
ЭН + ZrO₂ + TiO₂	24,75	1,05	4,03	0,30	0,18	—	—	—	16,9	1960	
Зерно фирмы «Тиролит»	21,63	0,27	1,45	0,55	0,17	—	—	—	14,1	2030	Извлечено из шлифкругов
Зерно фирмы «Нортон»	20,00	0,10	1,95	0,25	0,34	0.19	376	86,0	16,0	2290	

Table 2.23   Characteristics of zirconium electro corundum produced from different mixing materials

Column: 1. mixture [ЭК = EC, бадделеит = baddeleyite, Глинозем = alumina], granules from "Tirolit" company, granules from "Norton" company; 2. content of components by weight; 3. $\sigma_{e.g}$ (granularity 40), N/grain; 4. grain aggregation strength, %; 5. brittleness, %; 6. bulk density, kg/m³; 7. Note: a. laboratory samples, b. industrial batch, c. extracted from abrasion discs.

For the organisation of industrial production of zirconium electro corundum, it is essential to carry out research into new methods of crystallisation (pouring) and processing of fragments into abrasive materials.